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(54) Title: CATALYST SYSTEM OF ENHANCED PRODUCTIVITY

(57) Abstract

This invention relates to catalyst systems, and a method for using such system, for the enhanced production of homo and copolymer products of olefin, diolefin and/or acetylenically unsaturated monomers. This invention catalyst system comprises a Group III-A element compound for improving the productivity of an olefin polymerization catalyst which is the reaction product of a metallocene of a Group IV-B transition metal and an ionic activator compound comprising a cation capable of donating a proton and an anion which is bulky, labile and noncoordinateable with the Group IV transition metal cation produced upon reaction of the metallocene and activator compound to form the catalyst component of the catalyst system.

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TITLE: CATALYST SYSTEM OF ENHANCED PRODUCTIVITY

SPECIFICATION

Cross Reference to Related Applications

This application is a continuation-in-part of copending U.S. patent application Serial No. 133,480 filed December 22, 1987. U.S. Serial No. 133,480 is in turn a continuation-in-part of U.S. Serial No. 008,800 filed January 30, 1987.

Background of the Invention

1. Field of the Invention

This invention relates to the use of a Group III-A element compound for improving the productivity of an ionic metallocene olefin polymerization catalyst. This catalyst is the reaction product of a metallocene of a Group IV-B transition metal and an ionic activator compound comprising a cation capable of donating a proton and an anion which is bulky, labile and noncoordinating with the Group IV transition metal cation produced upon r action of the metallocene and activator compound to form the catalyst. Catalyst systems have enhanced productivity over similar catalysts not using Group IIIA compounds for the polymerization of olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers to polyolefins

having narrow molecular weight distributions and higher weight average molecular weights than heretofore attainable with a like metallocene which is activated to an active catalyst species by reaction with an aluminum alkyl or alumoxane cocatalyst.

2. Background

Ziegler-Natta type catalysts for the polymerization of olefins are well known. The traditional Ziegler-Natta type soluble systems comprise a metal halide activated to a catalyst species by reaction with a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. The activation of these traditional heterogeneous Ziegler-Natta catalysts generates a variety of different active sites. As a consequence of this non-uniformity of the active sites, the catalysts produce polymer products of undesirably broad molecular weight distribution (MWD). Furthermore, the polymer products exhibit poor composition distribution (CD), poor comonomer incorporation and poor sequence distribution.

Recently it has been found that active Ziegler-Natta type catalysts are formed when a bis(cyclopentadienyl) compound of the Group IV-B metals, including zirconium and hafnium, is activated by an alumoxane. The metallocene-alumoxane catalysts whether homogeneous or supported generally possess high activity and are versatile in that they may be effectively used to produce a variety of polymer products including, for example, high density linear polyethylene (HDPE), linear low density polyethylene (LLDPE), ethylene-propylene copolymer (EP), atactic polypropylene (a-PP) and isotactic polypropylene (i-PP). The metallocene-alumoxane catalysts also offer the significant advantage over the traditional Ziegler-Natta catalysts of being able to produce polymers with narrow MWD.

While the metallocene-alumoxane catalysts do offer significant advantages over the traditional Ziegler-Natta

catalysts, they nevertheless have limitations in practical commercial applications. These limitations include the relatively high cost of the alumoxane cocatalysts coupled with the high alumoxane requirements in practical applications. Furthermore, the metallocene-alumoxane catalysts, while producing a narrow MWD polymer product, have a limited capability to produce high molecular weight polymers or polymers having a high comonomer content. Alumoxane is also a pyrophoric composition thereby creating potential hazards in its handling and use. Finally, there is often an objectionably high content of aluminum in the product necessitating additional purifying process steps.

European Patent Application 277,004 (1988) describes a further advance in metallocene catalysts: a new metallocene catalyst which does not require either an alkyl aluminum or an alumoxane as an activator. The Group IV-B metallocene catalyst is prepared as a reaction product of a Group IV-B metal metallocene compound and an ionic activator compound. The ionic activator comprises a cation having a donatable proton and a labile, bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the activator cation donatable proton with a proton reactable substituent of a bis(cyclopentadienyl) Group IV-B metal compound to form a Group IV-B metal cation, the anion of the activator is sterically hindered from covalently coordinating to the Group IV-B metal cation. Hence, as described in our copending application, an active catalytic species of a metallocene is formed, namely an ionic pair comprising a m tallocene transition metal cation paired with a noncoordinating anion of the activator component.

The new metallocene catalyst system (hereafter referred to as an "ionic metallocene catalyst") eliminates

the need for an expensive alumoxane activator. The ionic metallocene catalyst also offers other advantages over the metallocene-alumoxane catalysts such as permitting the production of polyolefin products of narrow MWD and of significantly higher weight average molecular weight at high rates of catalytic activity while also permitting better incorporation of comonomers and the control of the chain end chemistry of the polymer products.

It is believed that the active catalytic species in the metallocene alumoxane catalysts is an ion pair. It is also believed that this ion pair active species is formed through a Lewis acid-Lewis base reaction of two neutral components (the metallocene and the alumoxane) leading to an equilibrium between a neutral, apparently catalytically inactive adduct, and an ion pair complex which is presumably the active catalyst. As a result of this equilibrium, there is a competition for the anion which must be present to stabilize the active Group IV-B metal cation of the active catalyst species. In the case of the ionic metallocene catalyst described herein, the metallocene and the activator react irreversibly and the equilibrium almost exclusively favors the catalytically active ion pair complex. Hence, the new ionic metallocene catalyst has a very high activity and is able to produce polyolefin products of high molecular weight and narrow molecular weight distribution.

Unfortunately, the active catalytic ion pair species of our ionic catalyst may irreversibly be inactivated by Lewis base impurities contained in the polymerization diluent or the monomer supply which which the ionic catalyst is used. The most prominent Lewis base impurities present in a polymerization diluent and/or a monomer are oxygen and water. Despite the most elaborate control, some, although minute, quantity of such Lewis base impurities will invariably be present in a polymerization diluent and/or the monomer supply. Consequently, with the new ionic catalyst, from which

aluminum alkyl and/or alumoxane has been eliminated as an activating cocatalyst, no reagent is present in the ionic catalyst to neutralize such impurities other than the ionic catalyst itself. Accordingly, some amount of the active catalyst species of the new ionic catalyst is consumed and deactivated by the neutralization of impurities in the polymerization diluent and/or monomer supply. Accordingly, the full rate of productivity inherent in our ionic catalyst composition has not yet been realized in practical application.

It would be desirable to discover an additive which could be used during polymerization which would neutralize impurities contained in the polymerization diluent and/or monomer supply without significantly affecting the ability of these ionic catalysts to produce superior polyolefin products of high weight average molecular weight, narrow molecular weight distribution, and high comonomer incorporation.

Summary of the Invention

The invention provides a catalyst system comprising an ionic metallocene catalyst and an additive which neutralizes deactivators of the ionic metallocene active sites. The catalyst system, like the ionic metallocene catalyst without additive disclosed in European Patent Application 277,004 (1988) (which is incorporated in full by reference), permits the production of polyolefins of high molecular weight and narrow molecular weight distribution (MWD). Moreover, the polyolefin products of the catalyst system have a narrow comonomer distribution (CD) approaching randomness and improved sequence distribution of comonomers as compared to the products of prior art metallocen -alumoxane supported catalysts. Further, like the ionic metallocene catalysts of the copending application, the catalyst systems are useful in the polymerization of olefins, diolefins, and/or acetylenically unsaturated monomers either alone or in

combination with each other. However, the addition of an additive which neutralizes those impurities capable of deactivating the active catalytic sites of the ionic metallocene catalyst provides a catalyst system of greatly improved productivity without significantly affecting molecular weight or extent of comonomer incorporation.

Since the invention's ionic metallocene catalyst component comprises the ionic metallocene catalyst of European Patent Application 277,004 (1988), the metallocene component of the catalyst may be selected from the bis(cyclopentadienyl) derivatives of a Group IV-B metal compound containing at least one ligand which will combine with an activator component or at least a portion thereof such as a cation portion thereof. The activator component of the catalyst is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group IV-B metal compound (metallocene component) and an anion which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom, which anion is bulky, labile and stable to any reaction involving the cation of the activator component. The charge-bearing metal or metalloid may be any metal or metalloid capable of forming a coordination complex which is not hydrolyzed by aqueous solutions. Upon combination of the metallocene component and activator component, the cation of the activator component reacts with one of the ligands of the metallocene component, thereby generating an ion pair consisting of a Group IV-B metal cation with a formal coordination number of 3 and a valence of +4 and the aforementioned anion, which anion is compatible with and noncoordinating toward the metal cation formed from the metallocene component. The anion of the activator compound must be capable of stabilizing the Group IV-B metal cation complex without interfering with the ability of the Gr up IV-B metal

cation or its decomposition product to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The selection of suitable metallocene-activator pairs to produce ionic metallocene catalysts is dealt with in European Patent Application 277,004 (1988).

The additive component of the catalyst system is a hydrolyzable Lewis acid able to neutralize those adventitious impurities such as moisture or oxygen which reduce the activity of the ionic metallocene catalyst component. These hydrolyzable Lewis acids should not be cocatalysts in themselves for the metallocene components of the ionic metallocene catalyst since this will result in more than one type of active site (ionic metallocene and metallocene-Lewis acid) thereby potentially adversely affecting the properties of the polymer product such as, for instance, the product MWD. Furthermore, the hydrolyzable Lewis acid should be compatible with the ionic metallocene catalyst and useful under the temperature and pressure conditions required for polymerization reactions. Thus, the useful Lewis acids comprise hydrocarbyl compounds of Group III-A metals.

Detailed Description of the Preferred Embodiments

As previously noted novel, metallocene based catalysts have been disclosed in European Patent Application 277,004 (1988) which are capable of producing polyolefin products, particularly polyethylene, and copolymers of ethylene and α-olefins, particularly ethylene-propylene copolymers, having greater weight average molecular weights at comparable or narrower molecular weight distributions than polyolefin products obtainable with a similar metallocene which is activated by an aluminum trialkyl or alumoxane cocatalyst. These novel metallocene based catalysts are referred to as "ionic metallocene catalysts."

This invention comprises the discovery that certain Group III-A element compounds may be used to prepare a catalyst system comprising an ionic metallocene catalyst which system has an enhanced rate of productivity, without significantly adversely effecting the advantageous properties of the polymer product producible with such ionic metallocene catalyst. With a catalyst system as described -- i.e., a system of an ionic metallocene catalyst and a Group III-A element compound additive to enhance productivity -- a polyolefin having the advantageous properties of high weight average molecular weight and narrow molecular weight distribution may be produced at a significantly reduced concentration of the ionic metallocene catalyst.

The catalyst system of the invention comprises an ionic metallocene catalyst and a Group III-A element compound. The process of the invention comprises the polymerization of one or more olefin monomers to a polyolefin product of high weight average molecular weight and narrow MWD in the presence of such catalyst system.

The Ionic Metallocene Catalyst

The ionic metallocene catalyst employed in accordance with the invention comprises the reaction product of a bis(cyclopentadienyl) Group IV-B metal compound having a proton reactable ligand and an ion exchange activator compound comprising a cation having a donatable proton and a labile, bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinating to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the donatable proton of the activator cation with the proton reactable ligand of the bis(cyclopentadienyl) Group IV-B metal compound to form a Group IV-B metal cation, the anion of the activator compound is sterically hindered from covalently coordinating to the Group IV-B metal cation,

and the lability of the activator anion is such that it is displaceable from said Group IV-B metal cation by an unsaturated hydrocarbon having a Lewis base strength equal to or greater than that of that of ethylene.

Metallocene Component of the
Ionic Metallocene Catalyst

The Group IV-B metal compounds, particularly the titanium, zirconium and hafnium compounds, useful as the metallocene component of the catalyst system employed in the process of this invention are bis(cyclopentadienyl) derivatives of titanium, zirconium or hafnium. In general, such useful titanium, zirconium and hafnium compounds may be represented by the following general formulae, in which "Cp" represents a cyclopentadienyl ring:

1. $(A\text{-}Cp)MX_1X_2$

2. $(A\text{-}Cp)M\overline{X'_1X'_2}$

3. $(A\text{-}Cp)ML$

4. $(Cp^*)(Cp\overline{R)M}X_1$

wherein: M is a Group IV-B metal namely titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radical and A' is a covalent bridging group containing a Group IV-A element; L is an olefin, diolefin or aryne ligand; each X_1 and X_2 independently, is a hydride radical, hydrocarbyl radical having from 1 to about 20 carbon atoms, substituted-hydrocarbyl radical having from 1 to about 20 carbon at ms wherein 1 or more of the hydrogen atoms are replaced with a halogen atom, organo-metalloid radical comprising a Group IV-A element

wherein each of the hydrocarbyl substituents contained in the organo portion of said organo-metalloid, independently, contain from 1 to about 20 carbon atoms; X'_1 and X'_2 are joined and bound to the metal atom to form a metallacycle, in which the metal, X'_1 and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and R is a substituent, preferably a hydrocarbyl substituent, having from 1 to 20 carbon atoms on one of the cyclopentadienyl radicals, which is also bound to the metal atom.

Each carbon atom in a cyclopentadienyl radical (Cp) may be, independently, unsubstituted or substituted with the same or a different hydrocarbyl radical, substituted-hydrocarbyl radical wherein one or more hydrogen atoms is replaced by a halogen atom, hydrocarbyl-substituted metalloid radical wherein the metalloid is selected from Group IV-A of the Periodic Table of the Elements, or halogen radical. Suitable hydrocarbyl and substituted-hydrocarbyl radicals which may be substituted for at least one hydrogen atom in the cyclopentadienyl radical contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Similarly, and when X_1 and/or X_2 is a hydrocarbyl or substituted-hydrocarbyl radical, each may, independently, contain from 1 to about 20 carbon atoms and be a straight or branched alkyl radical, a cyclic hydrocarbyl radical, an alkyl-substituted cyclic hydrocarbyl radical, an aromatic radical or an alkyl-substituted aromatic radical. Suitable organo-metalloid radicals include mono-, di- and trisubstituted organo-metalloid radicals of Group IV-A elements wherein each of the hydrocarbyl moieties contain from 1 to about 20 carbon atoms. Suitable organo-metalloid radicals include trimethylsilyl,

tri-ethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like.

Illustrative, but not limiting examples of bis(cylopentadienyl)zirconium compounds which may be used to prepare the catalyst component useful in the catalyst systems of this invention are dihydrocarbyl-substituted bis(cylopentadienyl)zirconium compounds such as bis(cylopentadienyl)zirconium dimethyl, bis(cylopentadienyl)zirconium diethyl, bis(cylopentadienyl)zirconium dipropyl, bis(cylopentadienyl)zirconium dibutyl, bis(cylopentadienyl)zirconium diphenyl, bis(cylopentadienyl)zirconium dineopentyl, bis(cylopentadienyl)zirconium di(m-tolyl), bis(cylopentadienyl)zirconium di(p-tolyl) and the like; (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds such as (methylcyclopentadienyl)(cyclopentadienyl) and bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclopentadienyl)(cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium dimethyl, (propylcyclopentadienyl)(cyclopentadienyl) and bis(propylcyclopentadienyl)zirconium dimethyl, (n-butylcyclopentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)zirconium dimethyl, (t-butylcyclopentadienyl)(cyclopentadienyl) and bis(t-butylcyclopentadienyl)zirconium dimethyl, (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl, (benzylcyclopentadienyl)(cyclopentadienyl) and bis(benzylcyclopentadienyl)zirconium dimethyl, (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and bis(diphenylmethylcyclopentadienyl)zirconium dimethyl, (methylcyclopentadienyl)(cyclopentadienyl) and bis(methylcyclopentadienyl)zirconium dihydride, (ethylcyclopentadienyl)(cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium dihydride,

(propylcyclopentadienyl)(cyclopentadienyl) and bis(propylcyclopentadienyl)zirconium dihydride, (n-butylcyclopentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)zirconium dihydride, (t-butylcyclopentadienyl)(cyclopentadienyl) and bis(t-butylcyclopentadienyl)zirconium dihydride, (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride, (benzylcyclopentadienyl)(cyclopentadienyl) and bis(benzylcyclopentadienyl)zirconium dihydride, (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like; (polyhydrocarbyl-substituted-cyclopentadienyl)zirconium compounds such as (dimethylcyclopentadienyl)(cyclopentadienyl) and bis(dimethylcyclopentadienyl)zirconium dimethyl, (trimethylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylcyclopentadienyl)zirconium dimethyl, (tetramethylcyclopentadienyl)(cyclopentadienyl) and bis(tetramethylcyclopentadienyl)zirconium dimethyl, (permethylcyclopentadienyl)(cyclopentadienyl) and bis(permethylcyclopentadienyl)zirconium dimethyl, (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl, (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl, (dimethylcyclopentadienyl)(cyclopentadienyl) and bis(dimethylcyclopentadienyl)zirconium dihydride, (trimethylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylcyclopentadienyl)zirconium dihydride, (tetramethylcyclopentadienyl)(cyclopentadienyl) and bis(tetramethylcyclopentadienyl)zirconium dihydride, (permethylcyclopentadienyl)(cyclopentadienyl) and bis(permethylcyclopentadienyl)zirconium dihydride, (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and bis(ethyltetramethylcyclopentadienyl)zirconium dihydride, (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium

dihydride and the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium compounds such as (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl, (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylgermylcyclopentadienyl)zirconium dimethyl, (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylstannylcyclopentadienyl)zirconium dimethyl, (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl, (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylsilylcyclopentadienyl)zirconium dihydride, (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylgermylcyclopentadienyl)zirconium dihydride, (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylstannylcyclopentadienyl)zirconium dihydride, (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and bis(trimethylplumblycyclopentadienyl)zirconium dihydride and the like; (halogen-substituted-cyclopentadienyl) zirconium compounds such as (trifluoromethylcyclopentadienyl) (cyclopentadienyl) and bis(trifluoromethylcyclopentadienyl)zirconium dimethyl (trifluoromethylcyclopentadienyl) (cyclopentadienyl) and bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the like; silyl-substituted bis(cyclopentadienyl)zirconium compounds such as bis(cyclopentadienyl)(trimethylsilyl)-(methyl)zirconium, bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium, bis(cyclopentadienyl) [tris(dimethylsilyl)silyl](methyl) zirconium, bis(cyclopentadienyl)-[bis(mesityl)silyl] (methyl)zirconium, bis-(cyclopentadienyl)(trimethylsilyl) trimethylsilylmethyl)zirconium, bis(cyclopentadienyl)(trimethylsilyl) benzyl) and the like; (bridged-cyclopentadienyl)zirconium compounds such

as methylene bis(cyclopentadienyl)zirconium dimethyl, ethylene bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl bis(cyclopentadienyl)zirconium dimethyl, methylene bis(cyclopentadienyl)zirconium dihydride, ethylene bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl bis(cyclopentadienyl)zirconium dihydride and the like; zirconacycles such as bis(pentamethylcyclopentadienyl) zirconacyclobutane, bis(pentamethylcyclopentadienyl) zirconacyclopentane, bis(cyclopentadienyl)zirconaindane and the like; olefin, diolefin and aryne ligand substituted bis(cyclopentadienyl)zirconium compounds such as bis(cyclopentadienyl)-(1,3-butadiene)zirconium, bis(cyclopentadienyl)-(2,3-dimethyl-1,3-butadiene)zirconium, bis(pentamethylcyclopentadienyl)(benzyne)zirconium and the like; (hydrocarbyl) (hydride) bis(cyclopentadienyl)zirconium compounds such as bis(pentamethylcyclopentadienyl)zirconium (phenyl) (hydride), bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the like; and bis(cyclopentadienyl) zirconium compounds in which a substituent on the cyclopentadienyl radical is bound to the metal such as (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylene) zirconium hydride, (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylene) zirconium phenyl and the like.

A similar list of illustrative bis(cyclopentadienyl) hafnium and bis(cyclopentadienyl)titanium compounds could be given, but since the lists would be nearly identical to that already presented with respect to bis(cyclopentadienyl)zirconium compounds, such listings of the analogous hafnium and titanium compounds are not deemed essential to a complete disclosure. Those skilled in the art, however, are aware that bis(cyclopentadienyl)hafnium compounds and bis(cyclopentadienyl)titanium compounds corresponding to certain of the listed bis(cyclopentadienyl)zirconium compounds are not known. The lists would, therefore, be

reduced by these compounds. Other bis(cyclopentadienyl)-hafnium compounds and other bis(cyclopentadienyl)titanium compounds as well as other bis(cyclopentadienyl)zirconium compounds which are useful in the catalyst compositions will, of course, be apparent to those skilled in the art.

Activator Compound of the Metallocene Catalyst

Compounds useful as an activator component in the preparation of the catalyst component of the catalyst system of this invention comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion containing a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group IV-B cation) which is formed when the metallocene and activator compounds are combined and said anion is sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Any metal or metalloid capable of forming a coordination complex which is stable in water may be used or contained in the anion of the activator compound. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Salts containing anions comprising a coordination complex containing a single boron atom are preferred.

In general, the activator compounds useful in the preparation of the catalysts may be represented by the following general formula:

5. $[(L'-H)^{+}]_d[(M')^{m+}Q_1Q_2\ldots Q_n]^{d-}$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and [L'-H] is a Bronsted acid;

M' is a metal or metalloid selected from the Groups subtended by Groups V-B to V-A of the Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

Q_1 to Q_n are, independently, hydride radical, dialkylamido radical, alkoxide radical, aryloxide radical, hydrocarbyl radical, substituted-hydrocarbyl radical or organometalloid radical and any one, but not more than one of Q_1 to Q_n may be a halide radical;

"m" is an integer from 1 to 7;

"n" is an integer from 2 to 8; and

n - m = "d".

The most preferred activator components for use in preparing the catalyst component of the catalyst system of this invention are those wherein the compatible noncoordinating anion is a complex containing a single metal or metalloid atom. Of such activator components, the most preferred for use are those containing a single boron atom in the anion. Activator compounds comprising boron which are particularly useful in the preparation of the catalyst may be represented by the following general formula:

5A. $[L'-H]^+[BAr_1Ar_2X_3X_4]^-$

wherein: L' is a neutral Lewis base, H is a hydrogen atom, and $[L'-H]^+$ is a Bronsted acid; B is boron in a valence state of 3; Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and X_3 and X_4 are independently, hydride radical, halide radical, provided that only one of X_3 or X_4 may be halide, hydrocarbyl radical containing from 1 to about 20 carbon atoms, substituted hydrocarbyl radical containing from 1 to about 20 carbon atoms wherein one or more f the

hydrogen atoms is replaced by a halogen atom, hydrocarbyl-substituted metal (organometalloid) radical wherein each hydrocarbyl substitution contains from 1 to about 20 carbon atoms and said metal is selected from Group IV-A of the Periodic Table of the Elements. Aromatic radicals suitable as the Ar_1 and Ar_2 groups include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents substituted aromatic hydrocarbon radicals suitable as the Ar_1 and Ar_2 groups, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy radicals, alkylamido radicals, fluoro and fluoro-hydrocarbyl radicals and the like. The substituent may be ortho, meta or para, relative to the carbon atom bonded to the boron atom. When either or both X_3 and X_4 are a hydrocarbyl radical, each may be the same or a different aromatic or substituted aromatic radical as are Ar_1 and Ar_3, or the same may be a straight or branched alkyl, alkenyl or alkynyl radical having from 1 to about 20 carbon atoms, a cyclic hydrocarbon radical having from about 5 to about 8 carbon atoms or an alkyl-substituted cyclic hydrocarbon radical having from about 6 to about 20 carbon atoms. X_3 and X_4 may also, independently, be an alkoxy or dialkylamido radical wherein the alkyl portion of said alkoxy and dialkylamido radical contains from 1 to about 20 carbon atoms; hydrocarbyl radical; or an organometalloid radical having from 1 to about 20 carbon atoms and the like. As indicated Ar_1 and Ar_2 may be linked to each other. Similarly, either or both of Ar_1 and Ar_2 could be linked to either X_3 or X_4. Finally, X_3 and X_4 may also be linked to each other through a suitable bridging group.

Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly compounds containing a single boron atom in the anion portion, are available commercially. In light

of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred activator components.

Illustrative, but not limiting, examples of activator components useful in preparing catalyst components utilized in the catalyst system and process of this invention wherein the activator anion is a coordination complex containing a single metal or metalloid atom are trialkyl-substituted ammonium salts such as triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-triflurormethylphenyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron and the like; N,N-dialkylanilinium salts such as N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium tetra(phenyl)boron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like; dialkyl ammonium salts such as di(i-propyl)ammonium tetra(pentafluorophenyl)boron, dicyclohexylammonium tetra(phenyl)boron and the like; and triarylphosphonium salts such as triphenylphosphonium tetra(phenyl)boron, tri(methylphenyl)phosphonium tetra(phenyl)boron, tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like.

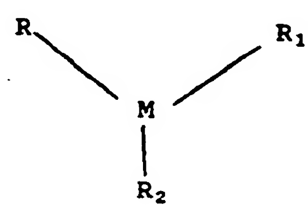
Similar lists of suitable compounds containing other metals and metalloids which are useful as activator components could be given, but such lists are not deemed necessary to a complete disclosure. In this regard, it should be noted that the foregoing list is not intended to be exhaustive and other boron compounds that would be useful, as well as useful activator compounds containing other metals or metalloids, would be readily apparent from

the foregoing general equations to those skilled in the art.

Group III-A Element Compound

Any solvent or diluent previously described as suitable for preparing the ionic metallocene catalyst is also suitable as a polymerization diluent for preparing catalyst systems of the invention.

Group III-A additive compounds suitable for use in preparing catalyst systems of the invention are represented by the following general formula:



wherein; M is a Group III-A element, preferably aluminum and boron; R, R_1 and R_2 are, independently, a straight or branched chain alkyl radical, a cyclic hydrocarbyl radical, an alkyl-substituted cyclohydrocarbyl radical, an aromatic radical or an alkyl-substituted radical of C_1 to C_{20} in carbon number. R_2 may also be an alkoxide radical of C_1 to C_{20} in carbon number.

Illustrative, but non-limiting, examples of Group III-A element compounds which are suitable are: when M is aluminum (Al) the trialkyl aluminums such as trimethyl aluminum, triethyl aluminum, tri-n-propyl aluminum, tri-isopropyl aluminum, tri-n-butyl aluminum, tri-sec-butyl aluminum, tri-t-butyl aluminum, tri-isobutyl aluminum, tri-n-pentyl aluminum, tri-isopentyl aluminum, tri-neopentyl aluminum, tricyclopentyl aluminum, tri-n-hexyl aluminum, tri-(4-methylpentyl) aluminum, tri-(3-methylpentyl) aluminum, tricyclohexyl aluminum, and the like; alkyl aluminums such as dimethylethyl aluminum, methyldiethyl aluminum, ethyldimethyl aluminum,

dimethyl-n-propyl aluminum, methyldi-n-propyl aluminum, dimethylisopropyl aluminum, dimethylcyclohexyl aluminum, methylethylpropyl aluminum, and the like; aryl and alkyl-substituted aluminums, such as triphenyl aluminum, tri-p-tolyl aluminum, tri-m-tolyl aluminum, tri-p-ethyl aluminum, and the like. Also suitable are aluminum alkoxides and aryloxides such as dimethyl aluminum methoxide, dimethyl aluminum ethoxide, diethyl aluminum ethoxide, diethyl aluminum isopropoxide, methyl ethyl aluminum methoxide, dimethyl aluminum 4-methylphenoxide, dimethyl aluminum 3-methylphenoxide, dimethyl aluminum 2,6-diisopropylphenoxide, dimethyl aluminum 2,6-di-t-butyl-4-methylphenoxide, and the like.

A similar list of illustrative Group III-A element compounds when M is boron could be made for the trialky boranes, alkyl boranes, and alkyl borane alkoxides. Also a similar list could be given for the analogous compounds of gallium and indium, although the gallium and indium analogies are much less preferred. Such list would be nearly identical to that already presented with respect to the aluminum species of Group III-A element compounds and therefore such listing of the borane analogous and other Group III-A elements analogous are not necessary to a complete disclosure.

Preferred Group III-A element compounds are those wherein M is aluminum or boron. Of the aluminum species of Group III-A element compounds, the most preferred are trialkylaluminums, and of the trialkylaluminums the most preferred are triethylaluminum and trimethylaluminum. Of the Group III-A element compounds wherein M is boron, the preferred boron species of Group III-A element compounds are trialkylboranes of which the most preferred is triethylborane.

When the catalyst system of the invention is to be employed for the production of polyethylene, the Group III-A element compound preferred for use in forming the catalyst system is triethylaluminum. When a catalyst

system of the invention is to be employed for the production of a copolymer, the Group III-A element compound preferred for use is a trialkylboron, most preferably triethylborane.

Depending upon the particular metallocene employed in preparing the ionic metallocene catalyst component of the catalyst system, and depending upon the nature of the polyolefin product to be prepared using such catalyst system, one type or species of Group III-A element compound may be more desirable than another.

<u>Choice of Metallocene-Activator Pairs</u>

In general, and while most metallocenes identified above may be combined with most activators identified above to produce an active olefin polymerization catalyst, it is important to continued polymerization operations that either a metal cation initially formed from the metallocene or a decomposition product thereof be a relatively stable catalyst. It is also important that the anion of the activator be stable to hydrolysis when an ammonium salt is used. Further, it is important that the acidity of the activator be sufficient, relative to the metallocene, to facilitate the needed proton transfer. Conversely, the basicity of the metal complex must also be sufficient to facilitate the needed proton transfer. Certain metallocene compounds - using bis(pentamethylcyclopentadienyl)hafnium dimethyl as an illustrative, but not limiting example - are resistant to reaction with all but the strongest Bronsted acids and thus are not suitable as metallocenes to form the catalysts of this invention. In general, bis(cyclopentadienyl)metal compounds which can be hydrolyzed by aqueous solutions can be considered suitable as metallocenes to form the catalysts described herein.

With respect to the combination of metallocenes to activators to form a catalyst of this invention, it should be noted that the two c mpounds combined for preparation

of the active catalyst must be selected so as to avoid transfer of a fragment of the anion, particularly an aryl group, to the metal cation, thereby forming a catalytically inactive species. This could be done by steric hindrance, resulting from substitutions on the cyclopentadienyl carbon atoms as well as substitutions on the aromatic carbon atoms of the anion. It follows, then, that metallocenes comprising perhydrocarbyl-substituted cyclopentadienyl radicals could be effectively used with a broader range of activators than could metallocenes comprising unsubstituted cyclopentadienyl radicals. As the amount and size of the substitutions on the cyclopentadienyl radicals are reduced, however, more effective catalysts are obtained with activators containing anions which are more resistant to degradation, such as those with substituents on the ortho positions of the phenyl rings. Another means of rendering the anion more resistant to degradation is afforded by fluorine substitution, especially perfluoro-substitution, in the anion. Fluoro-substituted stabilizing anions may, then, be used with a broader range of metallocenes.

While the inventors do not wish to be bound by any particular theory, it is believed that when the two compounds used to prepare the improved catalysts of the present invention are combined in a suitable solvent or diluent, all or a part of the cation of the activator (the acidic proton) combines with one of the substituents on the metallocenes. In the case where the metallocene has a formula corresponding to that of general formula 1, a neutral compound is liberated, which neutral compound either remains in solution or is liberated as a gas. In this regard, it should be noted that if either X_1 or X_2 in the metallocene is a hydride, hydrogen gas may be liberated. Similarly, if either X_1 or X_2 is a methyl radical, methane may be liberated as a gas. In the cases where the metallocene has a formula corresponding to those of general formulae 2, 3 or 4, one of the substituents on

the metallocene component is protonated but, in general, no substituent is liberated from the metal. It is preferred that the molar ratio of metallocene to activator be 1:1 or greater. The conjugate base of the cation of the second compound, if one remains, will be a neutral compound which will remain in solution or complex with the metal cation formed, though, in general an activator is chosen such that any binding of the neutral conjugate base to the metal cation will be weak or non-existent. Thus, as the steric bulk of this conjugate base increases, it will, simply, remain in solution without interfering with the active catalyst. Similarly, if the cation of the activator is a trialkyl ammonium ion, this ion will liberate a hydrogen atom to form gaseous hydrogen, methane or the like and the conjugate base of the cation will be a tertiary amine. In like fashion, if the cation were a hydrocarbyl-substituted phosphonium ion containing at least one reactive proton, as is essential to the present invention, the conjugate base of the cation would be a phosphine.

While still not wishing to be bound by any particular theory, it is also believed that as one of the metallocene substituents (a ligand) is liberated, the noncoordinating anion originally contained in the activator used in the catalyst preparation combines with and stabilizes either the metal cation formed from the metallocene, formally having a coordination number of 3 and a +4 valence, or a decomposition product thereof. The metal cation and noncoordinating anion will remain so combined until the catalyst is contacted with one or more olefins, diolefins, cyclic olefins and/or acetylenically unsaturated monomers either alone or in combination with one or more other monomers or another neutral Lewis base. As indicated supra, the anion contained in the activator must be sufficiently labile to permit rapid displacement by an olefin, diolefin, cyclic olefin or an acetylenically unsaturated monomer to facilitate polymerization.

The chemical reactions which occur in forming the catalysts of this invention may, when a preferred, boron containing compound is used as the activator, be represented by reference to the general formulae set forth herein as follows:

1. $(A\text{-}Cp)MX_1X_2 + [L'\text{-}H]^+[BAr_1Ar_2X_3X_4]^- \dashrightarrow$

$$[(A\text{-}Cp)MX_1]^+[BAr_1AR_2X_3X_4]^- + HX_2 + L' \text{ or}$$

$$[(A\text{-}Cp)MX_2]^+[BAr_1Ar_2X_3X_4]^- + HX_1 + L'$$

2. $(A\text{-}Cp)M\overline{X'_1X'_2} + [L'\text{-}H]^+[BAr_1Ar_2X_3X_4]^- \dashrightarrow$

$$[(A\text{-}Cp)M(\overline{X'_1X'_2}H)]^+[BAr_1AR_2X_3X_4]^- + L' \text{ or}$$

$$[(A\text{-}Cp)M(\overline{X'_2X'_1}H)]^+[BAr_1Ar_2X_3X_4]^- + L'$$

3. $(A\text{-}Cp)ML + [L'\text{-}H]^+[BAr_1AR_2X_3X_4]^- \dashrightarrow$

$$[(A\text{-}Cp)M(LH)]^+[BAr_1Ar_2X_3X_4]^- + L'$$

4. $(Cp)(\overline{R\text{-}Cp^*)M}X_1 + [L'\text{-}H]^+[BAr_1Ar_2X_3X_4]^- \dashrightarrow$

$$[Cp(HR\text{-}Cp^*)MX_1]^+[BAr_1AR_2X_3X_4]^- + L' \text{ or}$$

$$[Cp(\overline{R\text{-}Cp^*)M}]^+[BAr_1Ar_2X_3X_4]^- + HX_1 + L'$$

In the foregoing equations, the numbers correspond to the numbers set forth in combination with the general equations for useful metallocene compounds of Group IV-B metals. In general, the stability and rate of formation of the products in the foregoing reaction equations, particularly the metal cation, will vary depending upon the choice of the solvent, the acidity of the $[L'\text{-}H]^+$ selected, the particular L', the anion, the temperature at which the reaction is completed and the particular dicyclopentadienyl derivative of the metal selected. Generally, the initially formed ion-pair will be an active polymerization catalyst and will polymerize α-olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers either alone or in combination with other monomers. In some cases, however, the initial metal cation will decompose to yield an active polymerization catalyst.

As indicated supra, most metallocenes identified above will combine with most activators identified above to produce an active catalyst, particularly an active polymerization catalyst. The actual active catalyst species is not, however, always sufficiently stable as to permit its separation and subsequent identification. Moreover, and while many of the initial metal cations formed are relatively stable, it has become apparent that the initially formed metal cation frequently decomposes into one or more other catalytically active species.

While still not wishing to be bound by any particular theory, it is believed that the active catalyst species which have not been characterized, including active decomposition products, are of the same type as those which have been isolated and fully characterized or at least retain the essential ionic structure required for functioning as a catalyst. More particularly, it is believed that the active catalyst species which have not been isolated, including active decomposition products, are the same type as the isolated and characterized active catalyst species in that these species contain a bis(cyclopentadienyl)metal center which center remains cationic, unsaturated and has a metal-carbon bond which is reactive with olefins, diolefins, cylic olefins and acetylenically unsaturated compounds. Furthermore, it is believed that the decomposition products may react with hydrogen gas to enter into a common state of equilibrium involving the cationic hydride complex, $[Cp'CpMH]^{+}X^{-}$.

Polymerization Process

The process of this invention is one which polymerizes olefins, diolefins, cyclic olefins, and acetylenically unsaturated monomers to provide polyolefin homo and copolymers of narrow molecular weight distribution and higher weight average molecular weights than that heretofore attainable with a metallocene activated to an active catalyst species by an alkyl

aluminum or alumoxane cocatalyst. The process of this invention obtains such high molecular weight polyolefins at a rate of ionic metallocene catalyst productivity which is substantially greater than heretofore observed for a system of ionic metallocene catalyst.

The preferred polymerization process utilizing the invention catalyst system comprises the steps of: (1) contacting one or more monomers with a catalyst system comprising, in a polymerization diluent, the reaction product of a bis(cyclopentadienyl) Group IV-B metal compound and an activator compound -- each as previously described for the production of an ionic metallocene catalyst -- , and a Group III-A element compound -- as previously described --; (2) continuing the contact of such monomer with such catalyst system for a time sufficient to polymerize at least a portion of such monomer; and (3) recovering a polymer product.

In a preferred embodiment of the present invention, a bis(cyclopentadienyl)-Group IV-B metal compound containing two, independently, substituted or unsubstituted cyclopentadienyl radicals and one or two lower alkyl substituents and/or one or two hydride substituents will be combined with a tri-substituted ammonium salt of either a substituted or unsubstituted tetra(aromatic)boron. Each of the tri-substitutions in the ammonium cation will be the same or a different lower alkyl or aryl radical. By lower alkyl is meant an alkyl radical containing from 1 to 4 carbon atoms. When the bis(cyclopentadienyl)metal compound used is a bis(perhydrocarbyl-substituted cyclopentadienyl)metal compound, an unsubstituted or partially substituted tetra(aromatic)boron salt may be used. Tri(n-butyl)ammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(p-tolyl)boron and tri(n-butyl)ammonium tetra(p-ethylphenyl)boron are particularly preferred. As the number of hydrocarbyl-substitutions on the cyclopentadienyl radicals is reduced, however, substituted anions will be used in

the tri-substituted ammonium salts, particularly, pentafluoro-substituted anions. N,N-dimethyl-anilinium tetra(fluorophenyl)boron is particularly preferred.

Certain of the catalysts of this invention, particularly those based on hafnocenes - using the catalyst produced from the reaction of bis(cyclopentadienyl)hafnium dimethyl and the tri-substituted ammonium salt of tetra(pentafluorophenyl)boron as an example - when used as described herein for the polymerization and copolymerization of α-olefins, diolefins, and/or acetylenically unsaturated monomers, in the absence of a chain transfer agent, can lead to the production of extremely high molecular weight polymers and copolymers having relatively narrow molecular weight distributions. In this regard, it should be noted that homopolymers and copolymers having molecular weights up to about 2×10^6 or higher and molecular weight distributions within the range of about 1.5 to about 15 can be produced with the catalysts of this invention. The substituents of the cyclopentadienyl radicals, however, can exert a profound influence on polymer molecular weights and degree of comonomer incorporation.

The ionic metallocene catalysts containing a metallocene component which is either a pure enantiomer or the racemic mixture of two enantiomers of a rigid, chiral metallocene can polymerize prochiral olefins (propylene and higher α-olefins) to isotactic polymers. Bis(cyclopentadienyl)metal compounds in which each of the cyclopentadienyl radicals is substituted and containing a covalent bridging group between the two cyclopentadienyl radicals are particularly useful for isotactic polymerizations of this type. Prochiral metallocenes, for example these based on complexes of isopropyl-2-cyclopentadienyl-2-(1-fluorenyl) hafnium, can be used to polymerize propylene or higher α-olefins to syndiotactic polymers.

A particularly surprising feature of some of the ionic metallocene catalysts, particularly those based on hafnocenes in combination with an activator component comprising perfluorinated tetraphenylborate anions, is that when these catalysts are used to copolymerize α-olefins, either alone or in combination with diolefins, the amount of higher molecular weight olefin or diolefin incorporated into the copolymer is significantly increased when compared to copolymers prepared with the more conventional Ziegler-Natta type catalysts and bis(cyclopentadienyl)zirconium catalysts. The relative rates of reaction of ethylene and higher α-olefins with the aforementioned hafnium-based catalysts of this invention are much closer than with conventional Ziegler-Natta type catalysts of the Group IV-B metals. The comonomer distribution in copolymers prepared with the ionic metallocene catalysts, particularly with the lower α-olefins and lower diolefins, will range from near perfectly alternating to statistically random. Consequently, the hafnocene based ionic metallocene catalysts are particularly preferred.

While the ionic metallocene catalysts do not contain pyrophoric species, it is nevertheless preferred that the catalyst components be handled in an inert, moisture-free, oxygen-free environment such as argon, nitrogen, or helium because of the sensitivity of the catalyst components to moisture and oxygen. The Group III-A element compounds must also be handled in a similar manner.

In the preferred method, the metallocene and activator components are combined in a first step in an aromatic solvent to produce a solution of the ionic metallocene catalyst. This reaction may be carried out in the temperature range of about -100°C to about 300°C, preferably about 0° to about 100°C. Holding times to allow for th completion of the reaction may range from about 10 seconds to about 60 minutes depending upon

variables such as reaction temperature and choice of reactants.

Once the ionic metallocene catalyst component is formed, the order or method of addition of the Group III-A element compound to the polymerization diluent with ionic metallocene catalyst is not critical. That is, the catalyst system may be formed by: 1) first adding the Group III-A element compound to the polymerization diluent followed by addition of the ionic metallocene catalyst; 2) direct addition of the Group III-A element compound to a solution of ionic metallocene catalyst after which the common solution is added to a polymerization diluent; or 3) a portion of the Group III-A element compound may be added to a liquid monomer and supplied to the polymerization diluent containing ionic metallocene catalyst as the liquid monomer is supplied to the diluent. When a liquid monomer is used in the polymerization process, it is preferred to add the Group III-A element compound to the liquid monomer. The additive may be added neat or as a solution in a suitable hydrocarbon solvent, preferably an aliphatic or aromatic solvent.

Compared to an ionic metallocene catalyst in a polymerization diluent from which a Group III-A element compound is absent, the use of too great an amount of Group III-A element compound in forming a catalyst system of the invention will suppress the productivity of the ionic metallocene catalyst component. On the other hand, the use of too small an amount of Group III-A element compound will not produce an enhancement in productivity of the ionic metallocene catalyst system. The optimum amount of Group III-A element compound for use in producing catalyst systems of the invention is dependent, in part upon the amount of Lewis base impurities contained in the polymerization diluent and/or monomers used in polymerization. In a typical polymerization process, it is expected that the optimum amount of Group III-A element compound to be added to obtain a catalyst system of

maximum productivity will amount to a mole ratio of Group III-A element compound to activator compound of from about 1:1 to about 200:1, preferably 14:1 to 150:1.

For a given polymerization process, the optimum amount of Group III-A element compound to be added to a polymerization diluent in which an ionic metallocene catalyst component is present for forming a catalyst system of enhanced activity may readily be determined by monitoring the level of monomer consumption while adding the Group III-A element compound to the polymerization diluent until an amount of Group III-A element compound has been added which maximizes the rate at which the monitored monomer is consumed by the polymerization reaction. Alternatively, a portion of the Group III-A element compound is first added to the polymerization diluent after which the ionic metallocene catalyst is added and polymerization is initiated and the rate of monomer consumption is monitored. Then, while polymerization is ongoing, an additional quantity of the Group III-A element compound is added and the consumption is observed. It should, however, be borne in mind that the objective of adding the additive is to neutralize adventitious impurities such as water or oxygen so that the level of additive addition should also be proportioned to the level of impurities present. Thus, it may be advantageous to pretreat a monomer having a relatively high level of such impurities with the additive before the monomer is brought into contact with the catalyst system.

In general, the catalyst systems of this invention will polymerize olefins, diolefins and/or acetylenically unsaturated monomers either alone or in combination with other olefins and/or other unsaturated monomers at conditions well known in the prior art for conventional Ziegler-Natta catalysts.

Monomers which may be utilized in practice of the process include α-olefins, diolefins, and acetylenically unsaturated hydrocarbons containing from about 2 to about

18 carbon atoms. Such monomers include cyclic and acyclic hydrocarbons, and straight or branched chain hydrocarbons. Illustrative, and not limiting, of suitable monomers are: ethylene, propylene, 1-butene, 1-pentene, 1-hexane, 1-octene, 1-decene and the like; 2-methyl-1-propene, 3-methyl-1-butene, 2-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, and the like; 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene and the like; cyclopentene, cyclohexene, cycloheptene, and the like; propyne, butadyne, 1-4-hexadyne and the like.

In a most preferred embodiment of the present invention, bis(cyclopentadienyl)zirconium dimethyl or bis(cyclopentadienyl)hafnium dimethyl is reacted with N,N-dimethylanilinium tetra(pentafluorophenyl)boron to produce the most preferred ionic metallocene catalyst. The metallocene and activator are combined at a temperature within the range from about 0°C to about 100°C, preferably in an aliphatic hydrocarbon solvent, most preferably hexane or condensed propylene. Nominal holding times within the range from about 10 seconds to about 60 minutes are sufficient to produce the preferred ionic metallocene catalyst. The ionic metallocene catalyst is thereafter added to a polymerization diluent to which a Group III-A element compound, preferably triethylaluminum or triethylboron, has previously been added. The catalyst system so resulting is then, immediately after formation, used to polymerize a lower α-olefin, particularly ethylene or propylene, most preferably ethylene, at a temperature within the range from about 0°C to about 100°C, more preferably at from about 25 to 100°C, and at a pressure within the range from about 15 to about 500 psig. In a most preferred embodiment of the present invention, the most preferred catalyst system is used either to homopolymerize ethylene or to copolymerize ethylene with a lower α-olefin having from 3 to 6 carbon atoms, thereby yielding a plastic or an elastomeric copolymer. In both preferred process

embodiments, the monomers are maintained at polymerization conditions for a nominal holding time within the range from about 1 to about 60 minutes and the system is within the range from about 10^{-6} to about 10^{-5} moles of Group IV-B metal per liter of polymerization diluent, while a mole ratio of the Group III-A element compound to activator compound employed is maintained at from about 15:1 to about 150:1.

The use of the invention catalyst system which includes an additive for neutralizing impurities results in an improvement of from 20 to about 400% or more in ionic metallocene catalyst productivity over the ionic metallocene catalyst without the additive.

In general, catalyst systems can be tailored so as to produce polymer products which will be substantially freer of certain trace metals generally found in polymers produced with Ziegler-Natta type catalysts such as aluminum, magnesium, chloride and the like. Thus, for instance, the level of impurities may be monitored continuously and the rate of additive injection may be controlled to provide only that quantity of additive necessary to protect the catalyst sites from deactivation and not such an excess of additive so as to impair product quality or necessitate further processing to purify the polymer product. The polymer products produced with the invention ionic metallocene catalyst system have a broader range of applications than polymers produced with either the more conventional Ziegler-Natta type catalysts comprising a metal alkyl, such as an aluminum alkyl, or the metallocene-alumoxane catalysts which typically require an excess of the alumoxane catalyst.

The following examples serve to illustrate the invention and some of its advantages and are not intended to limit the scope of the invention as disclosed above or claimed hereafter.

EXAMPLES

Example 1

Ethylene was polymerized in a hexane diluent. Dry, oxygen-free hexane (400 ml) was added to a 1 liter stainless-steel autoclave previously flushed with nitrogen. Under nitrogen, a toluene solution (20 ml) containing 0.2 mmoles of triethylborane was transferred into the autoclave by means of a double-ended needle, followed by a solution of bis(cyclopentadienyl)zirconium dimethyl (3 mg) and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (1.5 mg) in toluene (5 ml). The autoclave was pressured with 90 psig of ethylene and stirred at 40°C. After 1 hour, the autoclave was vented and opened. The yield of linear polyethylene was 52.8 g. The polymer had a weight average molecular weight (M_w) of 449,000 with a molecular weight distribution (MWD) of 1.98. When the same procedure was followed except that no triethylborane was added, the yield of linear polyethylene was 13.3 g with a M_w of 455,000 and a MWD of 2.04.

Example 2

The procedure of Example 1 was repeated with the exception that a toluene solution (5 ml) containing bis(cyclopentadienyl)hafnium dimethyl (4 mg) and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (1.5 mg) was used. The yield of linear polyethylene was 24.6 g with a M_w of 1,424,000 and a MWD of 2.46. When the same procedure was followed except that no triethylborane was added, the yield of linear polyethylene was 3.5 g with a M_w of 485,000 and a MWD of 2.10.

Example 3

Ethylene was polymerized in a hexane diluent. Dry, oxygen-free hexane (400 ml) was added to a 1 liter stainless-steel autoclave previously flushed with nitrogen. Under nitrogen, a toluene solution (20 ml)

containing 0.2 mmoles of triethylborane was transferred into the autoclave by means of a double-ended needle. A catalyst solution of bis(cyclopentadienyl)hafnium dimethyl (18 mg) and N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (6 mg) in toluene (20 ml) was then injected into the autoclave by nitrogen pressure. The autoclave was pressured with 90 psig of ethylene and stirred at 40°C. After 30 minutes, the autoclave was vented and opened. The yield of linear polyethylene was 28.7 g. When the same procedure was followed except that no triethylborane was used, the yield of linear polyethylene was 12.6 g.

Comparative Example 3a

The procedure of Example 3 was repeated with the exception that a toluene solution (10 ml) containing triethylborane (0.1 mmole) was injected into the reactor first, followed by a toluene solution (30 ml) containing the catalyst of Example 3 and triethylborane (0.1 mmole). The yield of linear polyethylene was 30.9 g.

Comparative Example 3b

The procedure of Example 3 was repeated with the exception that triethylborane (0.2 mmoles) was contacted with the catalyst solution of Example 3 and the mixture injected into the autoclave. The yield of linear polyethylene was 33.3 g.

Example 4

The procedure of Example 1 was repeated using 20 ml of a toluene solution containing triethylaluminum (0.2 mmoles), followed by 10 ml of a toluene solution containing 3 mg of bis(cyclopentadienyl)zirconium dimethyl and 3 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron). The yield of linear polyethylene was 56.0 g with a M_w of 313,000 and a MWD of 2.52. When the same procedure was followed except that no

triethylaluminum was added, the linear polyethylene yield was 9.2 g with a M_w of 377,000 and a MWD of 2.54.

Example 5

The procedure of Example 4 was repeated with the exception that a toluene solution (20 ml) containing 3 mg bis(cyclopentadienyl)hafnium dimethyl and 6 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron) was used. The yield of linear polyethylene was 7.8 g as compared to zero yield in the absence of triethylaluminum when the same procedure was followed.

Comparative Example 5a

The procedure of Example 5 was repeated with the exception that 36 mg of bis(cyclopentadienyl)hafnium dimethyl was used and the N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron was omitted. No polyethylene was formed.

Example 6

The procedure of Example 1 was repeated using a toluene solution (20 ml) containing 0.2 mmole of tri-sec-butylborane, followed by 10 ml of a toluene solution containing 2 mg of bis(cyclopentadienyl)zirconium dimethyl and 6 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron). The yield of linear polyethylene was 2.12 g. The polymer had a M_w of 464,000 with a MWD of 2.08. When the same procedure was followed but no tri-sec-butylborane was added, the yield of linear polyethylene was 0.8 g with a M_w of 509,000 and a MWD of 2.06.

Example 7

The procedure of Example 6 was repeated with the exception that a toluene solution (10 ml) containing 3 mg of bis(cyclopentadienyl)hafnium dimethyl and 6 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron)

was used. The temperature rose to 52°C during the course of polymerization. The yield of linear polyethylene was 6.3 g. The polymer had a M_w of 835,000 and a MWD of 1.62. When the same procedure was followed but no tri-sec-butylborane was added, the yield of linear polyethylene was 1.7 g with a M_w of 884,000 and a MWD of 1.99.

Example 8

The procedure of Example 1 was repeated using a toluene solution (20 ml) containing 0.2 mmole trimethylaluminum, followed by a toluene solution (10 ml) containing 1 mg of bis(cyclopentadienyl)zirconium dimethyl and 3.5 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron. The yield of linear polyethylene was 40.4 g as compared to trace quantities when the same procedure was followed in the absence of trimethylaluminum.

Example 9

The procedure of Example 1 was repeated using 2 ml of a solution containing 1 ml of a 25.4 wt.% solution of diethylaluminum ethoxide diluted to 20 ml with toluene, followed by 10 ml of a toluene solution containing 4 mg of bis(cyclopentadienyl)zirconium dimethyl and 12 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron. The yield of linear polyethylene was 43 g as compared to no yield in the absence of diethylaluminum ethoxide when the same procedure was used.

Example 10

The procedure of Example 9 was repeated using a toluene solution (10 ml) containing 3 mg of bis(cyclopentadienyl)hafnium dimethyl and 6 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron. The yield of linear polyethylene was 4.75 g. The M_w of the polymer was 1,101,000 and the MWD was 1.55. When the

same procedure was followed in the absence of diethylaluminum, the yield of linear polyethylene was 4.0 g with a M_w of 899,000 and a MWD of 1.53.

Example 11

In this procedure, ethylene and propylene were copolymerized by adding, under a nitrogen atmosphere, 0.2 ml of a 25 wt.% solution of triethylaluminum in hexane followed by 10 ml of a toluene solution containing 36 mg of bis(cyclopentadienyl)hafnium dimethyl and 11 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron to a 1 liter stainless-steel autoclave previously flushed with nitrogen. Propylene (400 ml) was then added to the autoclave which was heated to 40°C and further pressurized with 200 psig of ethylene. After 30 minutes, the autoclave was vented and opened. The yield of ethylene-propylene copolymer was 65 g. The copolymer contained 67 wt.% ethylene, and had a molecular weight of 210,000 and a molecular weight distribution of 1.98. Under similar conditions, but in the absence of triethylaluminum, 37 grams of an ethylene-propylene copolymer were obtained with an ethylene content of 56 wt.%, a molecular weight of 548,000 and a molecular weight distribution of 1.66.

Example 12

The procedure of Example 11 was repeated using 0.2 mmole triethylborane, instead of the triethylaluminum, and a toluene solution (10 ml) containing 24 mg of bis(cyclopentadienyl)hafnium dimethyl and 8 mg of tetrakis(pentafluorophenyl)boron. The yield of ethylene-propylene copolymer was 10.8 g. The copolymer contained 60.8 wt.% ethylene, and had a M_w of 508,000 and a MWD of 1.74. Under similar conditions, but in the absence of triethylborane, 2.0 g of polymer were obtained with an ethylene content of 31.9 wt.%, a M_w of 541,000 and a MWD of 1.88.

The invention has been described with reference to its preferred embodiments. Those of skill in the art may appreciate from the description changes and modification which may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS:

1. A catalyst system for polymerizing ethylene, α-olefins, acetylenically unsaturated monomers and mixtures thereof, comprising, in a polymerizing diluent,

(a) a reaction product of

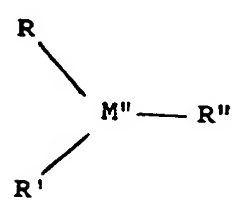
(i) a bis(cyclopentadienyl) Group IV-B metal compound having a proton reactable substituent; and

(ii) an activator compound comprising

(1) a cation having a donatable proton, and

(2) a labile, bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the cation donatable proton with the proton reactable substituent of said bis(cyclopentadienyl) Group IV-B metal compound whereby a Group IV-B metal cation is formed said anion is sterically hindered from covalently coordinating to the Group IV-B metal cation, and the lability of said anion being such that it is displaceable from said Group IVB metal cation by an unsaturated hydrocarbon having a Lewis base strength equal to or greater than ethylene; and

(b) A Group III-A element compound of the formula:



wherein M" is a Group III-A element, R, R', and R" are independently, a straight or branched chain alkyl radical of C_1-C_{20} in carbon number, and R' may be an alkoxide radical;

said Group IV-B metal compound and said activator compound being present in amounts sufficient to provide a catalytically active species; and said Group III-A element compound being present in an amount sufficient to neutralize adventitious impurities.

2. The catalyst system of claim 1 wherein the ratio of said activator compound to said Group IV-B metal compound is from about 1:1 to about 20:1.

3. The catalyst system of claim 2 wherein the ratio of said Group III-A element compound to said activator compound is from about 1:1 to about 100:1.

4. The catalyst system of claim 3, wherein said bis(cyclopentadienyl) Group IV-B metal compound is represented by one of the following general formulae:

1. $(A\text{-}Cp)MX_1X_2$

2. $(A\text{-}Cp)MX'_1X'_2$

3. $(A\text{-}Cp)ML$

4. $(Cp^*)(CpR)MX_1$

wherein: M is a Group IV-B metal;

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radical;

A' is a covalent bridging group;

L is an olefin, diolefin or aryne ligand;

X_1 and X_2 are, independently, hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, or organometalloid radical;

X'_1 and X'_2 are joined and bound to the M metal atom to form a metallacycle, in which the M metal atom, X'_1 and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and

R is a substituent on one cyclopentadienyl radical which is bound to the M metal atom.

5. The catalyst system of claim 4, wherein said activator compound is represented by the following general formula:

$$[(L'-H)^+]_d[(M')^{m+}Q_1Q_2\ldots Q_n]^{d-}$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and [L'-H] is a Bronsted acid;

M' is a metal or metalloid selected from Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

Q_1 to Q_n are, independently, hydride radical, dialkylamido radical, alkoxide radical, aryloxide radical, hydrocarbyl radical, substituted-hydrocarbyl radical or organometalloid radical and any one, but not more than one of Q_1 to Q_n a halide radical;

"m" is an integer from 1 to 7;

"n" is an integer from 2 to 8; and

n - m = "d".

6. The catalyst system of claim 5, wherein the Group III-A element compound comprises a trialkylaluminum, a trialkylborane, or mixtures thereof.

7. The catalyst system of claim 6, wherein said activator compound is represented by the following general formula:

$$[L'-H]^+[BAr_1Ar_2X_3X_4]^-$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and $[L'-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3;

Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals which radicals may be linked to each other through a stable bridging group; and X_3 and X_4 are, independently, hydride radical, halide radical, hydrocarbyl radical substituted-hydrocarbyl radical, or an organometalloid radical.

8. The catalyst of claim 7, wherein said Group IV-B metal compound is represented by the following general formula:

$$(A\text{-}Cp)MX_1X_2$$

wherein:

M is zirconium or hafnium;

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals;

A' is a covalent bridging group; and

X_1 and X_2 are, independently, hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, or an organometalloid radical.

9. The catalyst system of claim 8, wherein said activator compound is a trisubstituted ammonium salt of a substituted aromatic boron compound.

10. The catalyst system of claim 9, wherein said activator compound is tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron or N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

11. The catalyst system of claim 10, wherein the Group III-A element compound comprises a trialkylaluminum, a trialkylborane or mixtures thereof.

12. The catalyst system of claim 11, wherein the Group III-A element compound comprises triethylaluminum, trimethylaluminum or triethylborane.

13. The catalyst system of claim 12, wherein said activator compound is present in an amount to provide a mole ratio of activator compound to the Group IV metal compound of from about 1:1 to about 20:1 and said triethylaluminum is present in an amount to provide a mole ratio of triethylaluminum to activator compound of from about 1:1 to about 200:1.

14. The catalyst system of claim 12, wherein the Group III-A element compound is trimethylborane.

15. The catalyst system of claim 12, wherein said activator compound is present in an amount to provide a mole ratio of activator compound to the Group IV metal compound of from about 1:1 to about 20:1 and said trimethylborane is present in an amount to provide a mole ratio of trimethylborane to to activator compound of from about 1:1 to about 200:1.

16. The catalyst system of claims 12, 13, 14 and 15, wherein the Group IV-B metal compound is a bis(cyclopentadienyl) metal compound containing two, independently, substituted or unsubstituted cyclopentadienyl radicals and two lower alkyl substituents or two hydrides.

17. The catalyst system of claim 16, wherein said Group IV-B metal is zirconium.

18. The catalyst system of claim 16, wherein said Group IV-B metal is hafnium.

19. A method for polymerizing ethylene, α-olefins, acetylenically unsaturated monomers or mixtures of these monomers, comprising the steps of:

(I) contacting such monomer or monomer mixture with a catalyst system comprising, in a polymerization diluent,

(a) a reaction product of

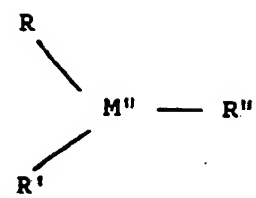
(i) a bis(cyclopentadienyl) Group IV-B metal compound having a proton reactable substituent; and

(ii) an activator compound comprising

(1) a cation having a donatable proton, and

(2) a labile, bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the cation donatable proton with the proton reactable substituent of said bis(cyclopentadienyl) Group IV-B metal compound whereby a Group IV-B metal cation is formed said anion is sterically hindered from covalently coordinating to the Group IV-B metal cation, and the lability of said anion being such that it is displaceable from said Group IV-B metal cation by an unsaturated hydrocarbon having a Lewis base strength equal to or greater than ethylene; and

(b) a Group III-A element compound of the formula:



wherein M" is a Group III-A element; R, R' and R" are independently, a straight or branched chain alkyl radical of C_1-C_{20} in carbon number, and R" may be an alkoxide radical; and

(II) continuing the contacting of step (I) for a sufficient period of time to polymerize at least a portion of the monomer; and

(III) recovering a polymer product.

20. The method of claim 19 wherein said contacting includes contacting with the reaction product of the activator and the Group IV-B metal compound in the ratio activator: Group IV-B metal compound from about 1:1 to about 20:1

21. The method of claim 20 wherein said contacting includes contacting in the ratio Group III-A element compound: activator from about 1:1 to about 200:1.

22. The method of claim 21, wherein said polymerization diluent is maintained at a temperature of from about 0 to about 100°C while continuing the contacting of step (I).

23. The method of of claim 22, wherein said bis(cyclopentadienyl) Group IV-B metal compound is represented by one of the following general formulae:

1. $(A\text{-}Cp)MX_1X_2$

2. $(A\text{-}Cp)M\overline{X'_1X'_2}$

3. (A-Cp)ML

4. $(Cp^*)(\overline{CpR})MX_1$

wherein: M is a Group IV-B metal;

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radical;

A' is a covalent bridging group;

L is an olefin, diolefin or aryne ligand;

X_1 and X_2 are, independently, hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, or organometalloid radical;

X'_1 and X'_2 are joined and bound to the M metal atom to form a metallacycle, in which the M metal atom, X'_1 and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and

R is a substituent on one cyclopentadienyl radical which is bound to the M metal atom.

24. The method of claim 23, wherein said activator compound is represented by the following general formula:

$$[(L'-H)^+]_d[(M')^{m+}Q_1Q_2\ldots Q_n]^{d-}$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and [L'-H] is a Bronsted acid;

M' is a metal or metalloid selected from Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

Q_1 to Q_n are, independently, hydride radical, dialkylamido radical, alkoxide radical, aryloxide radical, hydrocarbyl radical, substituted-hydrocarbyl radical or organometalloid radical and any one, but not more than one of Q_1 to Q_n a halide;

"m" is an integer from 1 to 7;

"n" is an integer from 2 to 8; and
$n - m =$ "d".

25. The method of claim 23, wherein the Group III-A element compound comprises a trialkylaluminum, a trialkylborane or mixtures thereof.

26. The method of claim 23, wherein said activator compound is represented by the following general formula:

$$[L'-H]^+[BAr_1Ar_2X_3X_4]^-$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and $[L'-H]^+$ is a Bronsted acid;
B is boron in a valence state of 3;
Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals which radicals may be linked to each other through a stable bridging group; and X_3 and X_4 are, independently, hydride radical, halide radical, hydrocarbyl radical substituted-hydrocarbyl radical, or an organometalloid radical.

27. The method of claim 26, wherein said Group IV-B metal compound is represented by the following general formula:

$$(A-Cp)MX_1X_2$$

wherein:

M is zirconium or hafnium;
(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals;
A' is a covalent bridging group; and
X_1 and X_2 are, independently, hydride radicals, hydrocarbyl radical, substituted-hydrocarbyl radical, or an organometalloid radical.

28. The method of claim 27, wherein said activator compound is a trisubstituted ammonium salt of a substituted aromatic boron compound.

29. The method of claim 28, wherein said activator compound is tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron or N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

30. The method of claim 29, wherein the Group III-A element compound is a trialkylaluminum or a trialkylborane.

31. The method of claim 30, wherein said Group IV-B metal is zirconium.

32. The method of claim 30, wherein said Group IV-B metal is hafnium.

AMENDED CLAIMS
[received by the International Bureau
on 10 September 1991 (10.09.91);
original claims 1, 6, 11, 12, 14, 19, 25 and 30 amended;
new claim 33 added; other claims unchanged (8 pages)]

1. A catalyst system for polymerizing ethylene, α-olefins, acetylenically unsaturated monomers and mixtures thereof, comprising, in a polymerizing diluent,

(a) a reaction product of

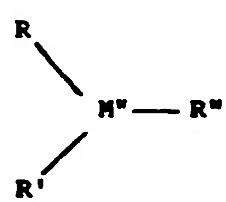
(i) a bis(cyclopentadienyl) Group IV-B metal compound having a proton reactable substituent; and

(ii) an activator compound comprising

(1) a cation having a donatable proton, and

(2) a labile, bulky anion which is a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, the bulk of said anion being such that upon reaction of the cation donatable proton with the proton reactable substituent of said bis(cyclopentadienyl) Group IV-B metal compound whereby a Group IV-B metal cation is formed said anion is sterically hindered from covalently coordinating to the Group IV-B metal cation, and the lability of said anion being such that it is displaceable from said Group IVB metal cation by an unsaturated hydrocarbon having a Lewis base strength equal to or greater than ethylene; and

(b) A hydrolyzable Lewis acid of the formula:



X_1 and X_2 are, independently, hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, or organometalloid radical;

X'_1 and X'_2 are joined and bound to the M metal atom to form a metallacycle, in which the M metal atom, X'_1 and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and

R is a substituent on one cyclopentadienyl radical which is bound to the M metal atom.

5. The catalyst system of claim 4, wherein said activator compound is represented by the following general formula:

$$[(L'-H)^+]_d[(M')^{m+}Q_1Q_2\ldots Q_n]^{d-}$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and [L'-H] is a Bronsted acid;

M' is a metal or metalloid selected from Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

Q_1 to Q_n are, independently, hydride radical, dialkylamido radical, alkoxide radical, aryloxide radical, hydrocarbyl radical, substituted-hydrocarbyl radical or organometalloid radical and any one, but not more than one of Q_1 to Q_n a halide radical;

"m" is an integer from 1 to 7;

"n" is an integer from 2 to 8; and

n - m = "d".

6. The catalyst system of claim 5, wherein the hydrolyzable Lewis acid comprises a trialkylaluminum, a trialkylborane, or mixtures thereof.

7. The catalyst system of claim 6, wherein said activator compound is represented by the following general formula:

$$[L'-H]^+[BAr_1Ar_2X_3X_4]^-$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and $[L'-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3;

Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals which radicals may be linked to each other through a stable bridging group; and X_3 and X_4 are, independently, hydride radical, halide radical, hydrocarbyl radical substituted-hydrocarbyl radical, or an organometalloid radical.

8. The catalyst of claim 7, wherein said Group IV-B metal compound is represented by the following general formula:

$$(A\text{-}Cp)MX_1X_2$$

wherein:

M is zirconium or hafnium;

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals;

A' is a covalent bridging group; and

X_1 and X_2 are, independently, hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, or an organometalloid radical.

9. The catalyst system of claim 8, wherein said activator compound is a trisubstituted ammonium salt of a substituted aromatic boron compound.

10. The catalyst system of claim 9, wherein said activator compound is tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron or N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron.

11. The catalyst system of claim 10, wherein the hydrolyzable Lewis acid comprises a trialkylaluminum, a trialkylborane or mixtures thereof.

12. The catalyst system of claim 11, wherein the hydrolyzable Lewis acid comprises triethylaluminum, trimethylaluminum or triethylborane.

13. The catalyst system of claim 12, wherein said activator compound is present in an amount to provide a mole ratio of activator compound to the Group IV metal compound of from about 1 :1 to about 20:1 and said triethylaluminum is present in an amount to provide a mole ratio of triethylaluminum to activator compound of from about 1:1 to about 200:1.

14. The catalyst system of claim 12, wherein the hydrolyzable Lewis acid is trimethylborane.

15. The catalyst system of claim 12, wherein said activator compound is present in an amount to provide a mole ratio of activator compound to the Group IV metal compound of from about 1:1 to about 20:1 and said trimethylborane is present in an amount to provide a mole ratio of trimethylborane to activator compound of from about 1:1 to about 200:1.

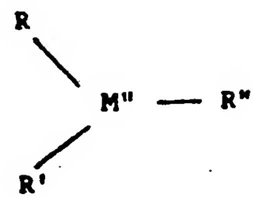
16. The catalyst system of claims 12, 13, 14. and 15, wherein the Group IV-B metal compound is a bis(cyclopentadienyl) metal compound containing two, independently, substituted or unsubstituted cyclopentadienyl radicals and two lower alkyl substituents or two hydrides.

17. The catalyst system of claim 16, wherein said Group IV-B metal is zirconium.

18. The catalyst system of claim 16, wherein said Group IV-B metal is hafnium.

19. A method for polymerizing ethylene, α-olefins, acetylenically unsaturated monomers or mixtures of these monomers, comprising the steps of:

(I) contacting such monomer or monomer mixture with an ionic polymerization catalyst comprising (i) a bis(cyclopentadienyl) derivative of a Group IV-B metal derived from a first compound having a metal center which is cationic, unsaturated and has a metal ligand bond which is reactive with olefins and/or diolefins and/or acetylenically unsaturated compounds with a coordination number of 3 and a 4+ valence combined with and stabilized by (ii) a non-coordinating anion derived from a second component which is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom which anion is bulky and stable to any reaction involving a cation of the second component used in reacting with at least one ligand of the first component, but sufficiently labile to permit displacement by an olefin and/or diolefin and/or diolefin and/or acetylenically unsaturated monomer during polymerization and (iii) a hydrolyzable Lewis acid, said Group IV-B metal derivative and said anion compound being present amounts sufficient to provide a catalytically active species; and said hydrolyzable Lewis acid being present in amounts sufficient to neutralize adventitious impurities.



(II) continuing the contacting of step (1) for a sufficient period of time to polymerize at least a portion of the monomer, thereby forming a polymer product.

20. The method of claim 19 wherein said contacting includes contacting with the reaction product of the activator and the Group IV-B metal compound in the ratio activator: Group IV-B metal compound from about 1:1 to about 20:1

21. The method of claim 20 wherein said contacting includes contacting in the ratio Group III-A element compound: activator from about 1:1 to about 200:1.

22. The method of claim 21, wherein said polymerization diluent is maintained at a temperature of from about 0 to about 100° C while continuing the contacting of step (I).

23. The method of claim 22, wherein said bis(cyclopentadienyl) Group IV-B metal compound is represented by one of the following general formulae:

1. $(A\text{-}Cp)MX_1X_2$

2. $(A\text{-}Cp)MX'_1X'_2$

"n" is an integer from 2 to 8; and
$n - m =$ "d".

25. The method of claim 23, wherein the hydrolyzable Lewis acid comprises a trialkylaluminum, a trialkylborane or mixtures thereof.

26. The method of claim 23, wherein said activator compound is represented by the following general formula:

$$[L'\text{-}H]^+[BAr_1Ar_2X_3X_4]^-$$

wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and
$[L'\text{-}H]+$ is a Bronsted acid;
B is boron in a valence state of 3;
Ar_1 and Ar_2 are the same or different aromatic or substitued-aromatic hydrocarbon radicals which radicals may be linked to each other through a stable bridging group; and X_3 and X_4 are, independently, hydride radical, halide radical, hydrocarbyl radical substituted-hydrocarbyl radical, or an organometalloid radical.

27. The method of claim 26, wherein said Group IV-B metal compound is represented by the following general formula:

$$(A\text{-}Cp)MX_1X_2$$

wherein:

M is zirconium or hafnium;
(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals;
A' is a covalent bridging group; and
X_1 and X_2 are, independently, hydride radicals, hydrocarbyl radical, substituted-hydrocarbyl radical, or an organometalloid radical.

28. The method of claim 27, wherein said activator compound is a trisubstituted ammonium salt of a substituted aromatic boron compound.

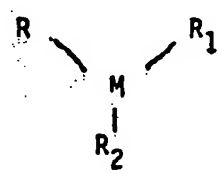
29. The method of claim 28, wherein said activator compound is tri(n-butyl) ammonium tetrakis(pentafluorophenyl)boron or N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron .

30. The method of claim 29, wherein the hydrolyzable Lewis acid is a trialkylaluminum or a trialkylborane.

31. The method of claim 30, wherein said Group IV-B metal is zirconium.

32. The method of claim 30, wherein said Group VI-B metal is hafnium.

33. The catalyst according to claim 1 wherein the hydrolyzable Lewis acid is a Group III-A element compound of the formula



wherein M is a Group III-A element; R, R_1, and R_2 are, independently, a straight or branched-chain alkyl radical, a cyclic hydrocarbyl radical, an alkyl-substituted cyclohydrocarbyl radical, or an aromatic radical, or R_2 may be an alkoxide or aryloxide radical.

STATEMENT UNDER ARTICLE 19

The following European Patent Applications have been cited in the International Search Report as being of particular relevance to the claimed invention: EPA-A-1 0277 004 and EPA-A-1 0277 003. It has been stated that both the claims and examples of these cited references are relevant to claims 1 through 32 of the subject application making the claimed invention be considered not novel or inventive. It is respectfully traversed that these cited references make the subject invention not novel or inventive.

EPA '004 has been cited in the subject application on pages 3 and 4 of the specification.

EPA '004 describes an ionic pair catalyst useful for the production of polyolefin products of narrow molecular weight distribution and high weight average molecular weights. As stated on page 4, lines 27 of the subject application, the ionic catalyst described in EPA '004 contained the disadvantage of being able to be irreversibly inactivated by Lewis bases impurities. These impurities are often contained in the polymerization diluent or the monomer supply with which the ionic catalyst is used. The examples and the claims of EPA '004 are directed to a method for preparing a catalyst comprising the steps of combining at least one first component consisting of a bis-cyclopentadienyl metal compound with a second compound comprising a cation and a anion species. Contacting of the two components species must continue for a sufficient period of time to permit the cation of the second component to react with a substituent in the bis(cyclopentadienyl) metal compound.

Due to the ability of Lewis base impurities to irreversibly inactivate the ionic pair catalyst described in '004, an objective of the subject application was to locate an additive which would neutralize impurities without effecting the ability of the catalyst to produce high molecular weight, narrow molecular weight distribution and high comonomer incorporation of polyolefin products. All claims and examples illustrated in EPA '004 are directed merely to the production and use thereof of the ionic pair catalyst without an additive to eliminate the inactivation possibility of the catalyst system.

EPA 0277 003, assigned to the assignee of record for the subject application, and by the same inventors, describes a method of producing an ionic pair catalyst. The anion of said ionic pair catalyst contains a plurality of boron atoms which function to stabilize the cation species of said catalyst. The examples and claims of EPA '003 are directed to an anion system containing a plurality of boron atoms and do not contain any reference to an ionic pair catalyst system containing a hydrolyzable Lewis acid such as a Group III-A element.

The hydrolyzable Lewis acid or Group III-A element is utilized as a scavenger or additive to neutralize the deactivators of the ionic metallocene active sites. This hydrolyzable Lewis acid enhances productivity of the ionic pair metallocene catalyst by scavenging any type of moisture which can be found in the form of oxygen or water present in the polymerization diluent or the monomer supply.

The subject application is an improvement over EPA 277 004 or EPA 277 003. The improvement consists of the hydrolyzable Lewis acid (Group III-A element) additive to enhance the productivity of the ionic pair and neutralize any possible deactivators such as oxygen or water which may decrease the activity or the active sites of the ionic pair catalyst for the production of narrow molecular weight distribution or high average molecular weight polyolefin products.

The inventive step found in the subject application is the additive which is able to neutralize any deactivators which may be present during the polymerization of polyolefin products.

It is respectfully submitted that the references cited and applied against the subject application are relevant for defining the general state of the art (eg ionic metallocene catalyst) however they are not relevant as against the subject application to eliminate the novelty or the inventive step of the claimed invention.